

What is claimed is:

1. A method of forming a conversion layer on a metallic surface comprising the steps of:
- 5 treating the metallic surface with an aqueous treating solution comprising:
- (a) a source of tungstate ions; and
 - (b) a soluble material comprising zirconium; and
- thereafter drying and/or baking the treated metal surface.
- 10 2. A method according to claim 1, wherein the aqueous treating solution further comprises ammonium hydroxide.
3. A method according to claim 1, wherein the source of tungstate ions is selected from the group consisting of ortho-tungstates, meta-tungstates and para-tungstates,
- 15 polytungstates, heteropolytungstates, isopolytungstates, peroxytungstates, and combinations thereof.
4. A method according to claim 3, wherein the source of tungstate ions is meta-tungstate or para-tungstate.
- 20 5. A method according to claim 3, wherein the source of tungstate ions is selected from the group consisting of sodium, potassium, lithium, calcium, cerium, barium, magnesium, strontium, hydrogen and ammonium tungstate salts.
- 25 6. A method according to claim 3, wherein the source of tungstate ions is tungstic acid, hexaammonium salt.
7. A method according to claim 1, wherein the concentration of tungstate ions, measured as tungsten, in treating solution is about 0.01 g/l to about 10.0 g/l.
- 30 8. A method according to claim 7, wherein the concentration of tungstate ions, measured as tungsten, in the treating solution is about 0.1 g/l to about 1.5 g/l.

9. A method according to claim 8, wherein the concentration of tungstate ions, measured as tungsten, in the treating solution is 1.0 g/l.
10. A method according to claim 1, wherein the soluble material comprising zirconium is selected from the group consisting of zirconium ammonium fluoride, dihydrogen hexafluorozirconate, potassium hexafluorozirconate, zirconium sulfate, zirconium carbonate, zirconium nitrate, and zirconium phosphate.
11. A method according to claim 10, wherein the soluble material comprising zirconium is dihydrogen hexafluorozirconate.
12. A method according to claim 1, wherein the concentration of the soluble material comprising zirconium in the treating solution is about 0.01 g/l to about 2.0 g/l.
13. A method according to claim 12, wherein the concentration of the soluble material comprising zirconium in the treating solution is about 0.05 g/l to about 0.5 g/l.
14. A method according to claim 1, wherein the aqueous treating solution further comprises a soluble aluminum salt.
15. A method according to claim 14, wherein the concentration of the soluble aluminum salt is between 5 and 500 parts per million as aluminum.
16. A method according to claim 1, wherein the temperature of the treating solution is within the range of about 55°F to about 180°F.
17. A method according to claim 16, wherein the temperature of the treating solution is about 70°F to about 120°F.
18. A method according to claim 1, wherein the pH of the treating solution is maintained from about 2.8 to about 7.0.

19. A method according to claim 1, wherein the parts are cleaned prior to treating the metallic surface with the treating solution.
20. A method according to claim 19, wherein the metallic surface is deoxidized after
5 cleaning and prior to treating with the treating solution.
21. A method according to claim 1, wherein the treating solution is free of chromium.
22. A method according to claim 1, wherein the treating solution is applied by
10 immersion or by spraying.
23. A method according to claim 1, wherein the treating solution further comprises at least one of a surfactant, an accelerator, a dye, an organic polymer, a buffering agent, and a pH adjusting agent.
- 15 24. An aqueous conversion coating composition comprising a source of tungstate ions and a soluble material comprising zirconium.
25. A composition according to claim 24, wherein the aqueous treating solution
20 further comprises ammonium hydroxide.
26. A composition according to claim 24, wherein the source of tungstate ions is selected from the group consisting of ortho-tungstates, meta-tungstates and para-tungstates, polytungstates, heteropolytungstates, isopolytungstates, peroxytungstates, and
25 combinations thereof.
27. A composition according to claim 26, wherein the source of tungstate ions is meta-tungstate or para-tungstate.
- 30 28. A composition according to claim 26, wherein the source of tungstate ions is selected from the group consisting of sodium, potassium, lithium, calcium, cerium, barium, magnesium, strontium, hydrogen and ammonium tungstate salts.

29. A composition according to claim 26, wherein the source of tungstate ions is tungstic acid, hexaammonium salt.
30. A composition according to claim 24, wherein the concentration of tungstate ions, measured as tungsten, in treating solution is about 0.01 g/l to about 10.0 g/l.
31. A composition according to claim 30, wherein the concentration of tungstate ions, measured as tungsten, in the treating solution is about 0.1 g/l to about 1.5 g/l.
32. A composition according to claim 31, wherein the concentration of tungstate ions, measured as tungsten, in the treating solution is 1.0 g/l.
33. A composition according to claim 24, wherein the soluble material comprising zirconium is selected from the group consisting of zirconium ammonium fluoride, dihydrogen hexafluorozirconate, potassium hexafluorozirconate, zirconium sulfate, zirconium carbonate, zirconium nitrate, and zirconium phosphate.
34. A composition according to claim 33, wherein the soluble material comprising zirconium is dihydrogen hexafluorozirconate.
35. A composition according to claim 24, wherein the concentration of the soluble material comprising zirconium in the treating solution is about 0.01 g/l to about 2.0 g/l.
36. A composition according to claim 35, wherein the concentration of the soluble material comprising zirconium in the treating solution is about 0.05 g/l to about 0.5 g/l.
37. A composition according to claim 24, wherein the aqueous treating solution further comprises a soluble aluminum salt.
38. A composition according to claim 37, wherein the concentration of the soluble aluminum salt is between 5 and 500 parts per million as aluminum.

39. A composition according to claim 24, wherein the temperature of the treating solution is within the range of about 55°F to about 180°F.

5 40. A composition according to claim 39, wherein the temperature of the treating solution is about 70°F to about 120°F.

41. A composition according to claim 24, wherein the pH of the treating solution is maintained from about 2.8 to about 7.0.

10 42. A composition according to claim 24, wherein the treating solution is free of chromium.

15 43. A composition according to claim 24, wherein the treating solution further comprises at least one of a surfactant, an accelerator, a dye, an organic polymer, a buffering agent, and a pH adjusting agent.